

Contamination of the Bay of Fundy—Gulf of Maine area with Polychlorinated Biphenyls, Polychlorinated Terphenyls, Chlorinated Dibenzodioxins, and Dibenzofurans

by V. Zitko*, O. Hutzinger†, and P. M. K. Choi**

The procedure used to determine polychlorinated biphenyls (PCBs), polychlorinated terphenyls (PCTs), chlorinated dibenzodioxins, and chlorinated dibenzofurans is outlined in Table 1. It is based on the cleanup-chromatography of Holden and Marsden (1), modified as described (2). Most PCBs are eluted in fraction I. Fraction II contains some PCBs, p,p'-DDE, and PCTs, whereas heptachlor epoxide, dieldrin, endrin, p,p'-DDD, and p,p'-DDT are eluted in fraction III. Fractions I and II are further chromatographed on alumina, essentially according to Porter and Burke (3), to determine chlorinated dibenzodioxins and dibenzofurans.

PCTs, hexa- and octachlorodibenzodioxin, and octachlorodibenzofuran were quantified by gas chromatography on 3% OV-210 on Chromosorb WAW 60/80 in a 6 ft × 4 mm column at 200°C. A 4% SE-30 column was used to quantify PCBs, chlorinated hydrocarbon pesticides, 2,3,7,8-tetrachlorodibenzodioxin, di-, tri-, and tetrachlorodibenzofuran.

Recovery of PCBs and chlorinated hydrocarbon

pesticides in this procedure was generally better than 95% (2). Recovery of PCTs was 90%. Results of the analyses of commercial fishmeal, spiked with chlorinated dibenzodioxins and dibenzofurans are presented in Table 2.

PCTs were found only in eggs and fatty tissues of herring gulls in levels of 0.1 and 1.4 µg/g wet weight, expressed as Aroclor 5460, respectively. This indicates that PCTs are not as widely spread in the environment as PCBs.

Only a limited number of samples were analyzed for chlorinated dibenzodioxins and dibenzofurans. The samples included muscle and liver of white shark (*Carcharodon carcharias*), eggs of double-crested cormorants (*Phalacrocorax auritus*), and herring gulls (*Larus argentatus*), commercial herring oil, and groundfish herring fishmeal. No residues of chlorinated dibenzodioxins and dibenzofurans were found.

Detection limits of the individual compounds are estimated in Table 3.

The absence of chlorinated dibenzodioxins and dibenzofurans from aquatic animals is encouraging. However, these compounds are extremely toxic, and a more detailed investigation is necessary. The analytical technique should be further improved to achieve lower detection limits.

The levels of PCBs and chlorinated hydrocarbon pesticides found in fishes, double-crested

* Environment Canada, Fisheries Research Board, Biological Station, St. Andrews, New Brunswick.

† Atlantic Regional Laboratory, National Research Council of Canada, Halifax, Nova Scotia.

** McMaster University, Hamilton, Ontario, Canada.

Table 1. Procedure for determining PCBs, PCTs, chlorinated dibenzodioxins, and chlorinated dibenzofurans.

Chromatography on alumina
(800°C 4 h, 5% H₂O)

Chromatography on Silicar^R
(130°C overnight, 3% H₂O)

Fraction I (10 ml hexane)

Fraction I I (20 ml 2% CH₂Cl₂
in hexane)

PCB, C₆Cl₆

Fraction I II (10 ml 20% CH₂Cl₂
in hexane)

HCDD faster isomer,
TCDD, OCDD, OCDF

Chromatography on alumina
(130°C overnight)

Fraction II I (20 ml 2% CH₂Cl₂
in hexane)

p,p'-DDE

Fraction II (20 ml hexane)

Fraction II II (10 ml 20%
CH₂Cl₂ in hexane)

HCDD slower isomer,
TCDD, CDF

Fraction III (10 ml 10% ether in hexane)

TCDD = 2, 3, 7, 8-tetrachlorodibenzodioxin.

HCDD, OCDD = hexa-, octachlorodibenzodioxin.

CDF = mixture of di-, tri-, and tetrachlorodibenzofuran.

OCDF = octachlorodibenzofuran.

cormorants, and herring gulls from the Bay of Fundy-Gulf of Maine area are summarized in Table 4. The concentration of PCBs is generally higher than that reported for the same or similar species from other areas, such as the Baltic Sea (4), California coastal waters (5), Britain (6), and Western Canada (7).

It is interesting to note that the levels of PCBs found in fishes from the Bay of Fundy-Gulf of

Maine area are about one order of magnitude higher than those in fishes from the Nova Scotia banks (2). Determination of PCB residues in Atlantic salmon (*Salmo salar*) also indicates that elevated levels of PCBs are associated with coastal areas. Thus muscle of salmon caught off Greenland contains 0.20 µg/g of PCBs, whereas in specimens landed in Canada PCB levels are from 0.45 to 0.62 µg/g on wet weight basis.

In all samples the peak pattern of PCB residues resembles quite closely that of Aroclor 1254, and the results are expressed as Aroclor 1254. However, fish from lower and intermediate levels of the food web contain relatively lower amounts of hexachlorobiphenyls (4th, 5th, and 6th major Aroclor 1254 peak) and higher amounts of tetra- and

Table 2. Analysis of spiked fishmeal samples, µg/g wet weight.

Sample	TCDD*		HCDD*		OCDD*	
	Added	Found	Added	Found	Added	Found
1	1.18	0.96	1.08	1.15	1.30	1.29
2	0.59	0.64	1.08	1.04	0.65	0.57
3	0.29	0.33	0.26	0.31	0.32	0.50

	CDF*		OCDF*	
	Added	Found	Added	Found
4	1.21	1.41	0.91	0.96
5	0.60	0.62	0.45	0.38
6	0.30	0.28	0.23	0.14

* See Table 1.

Table 3. Detection limits of chlorinated dibenzodioxins and dibenzofurans

Compound	Detection limit, µg/g wet weight
TCDD*	0.04
CDF*	0.02
HCDD*	0.02
OCDD*	0.01
OCDF*	0.01

* See Table 1.

Table 4. PCB and chlorinated hydrocarbon pesticides in aquatic animals from the Bay of Fundy-Gulf of Maine area.

Species	Tissue	PCBs (as Aroclor 1254)	µg/g wet weight p,p'-DDE	Other
Herring <i>Clupea harengus</i>	whole fish	0.34	0.06	
Mackerel <i>Scomber scombrus</i>	muscle	0.35	0.07	
Plaice <i>Hippoglossoides platessoides</i>	muscle	0.38	0.01	
White hake <i>Urophycis tenuis</i>	muscle	0.44	0.03	
Ocean perch <i>Sebastes marinus</i>	muscle	0.32	0.03	
Cod <i>Gadus morhua</i>	muscle	0.55	0.04	
Sea raven <i>Hemitripterus americanus</i>	muscle	0.21	0.08	DDT 0.24
	viscera	0.73	0.30	
Basking shark <i>Cetorhinus maximus</i>	muscle	0.07	—	
	liver	1.07		
White shark <i>Carcharodon carcharias</i>	muscle	0.77	0.48	
	liver	218	335	DDT 63 DDD 43
Bluefin tuna <i>Thunnus thynnus</i>	muscle	1.54	0.15	
Herring oil		3.55	2.27	DDT 0.37
Fishmeal		0.54	0.19	
Double-crested cormorant	eggs	43.5*	29.4*	
<i>Phalacrocorax auritus</i>		17.2*	8.6*	
	muscle	3.38	8.40	
	liver	2.13	4.16	
	Subcut. fat	38	164	
	Abdom. fat	52	162	
Herring gull <i>Larus argentatus</i>	eggs	12.6*	5.67*	
		5.54*	2.83*	
	muscle liver	5.06	2.07	
		6.50	2.08	
	Subcut. fat	75	26	

* Different nesting colonies.

pentachlorobiphenyls (1st and 2nd major Aroclor 1254 peak) than high trophic level white and silky shark (*Carcharodon carcharias* and *Carcharhinus falciformis*, respectively) and aquatic birds. Atlantic salmon parr fed Aroclor 1254-contaminated diet in the laboratory also contain relatively higher amounts of tetra- and pentachlorobiphenyls. This may indicate that fish more efficiently absorb the lower chlorinated biphenyls. On the other hand, these compounds may be metabolized and excreted, so that a preferential accumulation of higher chlorinated biphenyls occurs in the food chains. The fractions of hexachlorobiphenyls at different trophic levels are summarized in Table 5.

The toxicological significance of environmental levels of PCBs and their rate of accumulation in the environment are not known. In spite of this, PCBs and other industrial halogenated hydrocarbons should be considered potentially harmful,

Table 5. Fraction of hexachlorobiphenyls at different trophic levels.

Sample	Fraction of hexachloro- biphenyls in terms of Aroclor 1254 peak heights, ^a
	$\frac{4+5+6}{1+2+4+5+6}$
Aroclor 1254	0.56
Fish, wild	0.38
Atlantic salmon parr on Aroclor 1254- contaminated diet	0.41
Silky shark	0.74
White shark	0.71
Eggs of double-crested cormorants and herring gulls	0.72

^a Numbers refer to the major Aroclor 1254 peaks.

and their release into the environment should be limited as much as possible.

Acknowledgments

We thank our colleagues at the Biological Station, St. Andrews, New Brunswick, Canada, for samples of fish and Dr. D. Firestone, Food and Drug Administration, Washington, D.C., U.S.A., for samples of chlorinated dibenzodioxins and dibenzofurans. We thank Mrs. Madelyn M. Irwin for typing the manuscript.

REFERENCES

1. Holden, A. V. and Marsden, K. 1969. Single-stage clean-up of animal tissue extracts for organochlorine residue analysis. *J. Chromatogr.* 44: 481.
2. Zitko, V. 1971. Polychlorinated biphenyls and organochlorine pesticides in some freshwater and marine fishes. *Bull. Environ. Contamin. Toxicol.* 6: 464.
3. Porter, M. L. and Burke, J. A. 1971. Separation of three chlorodibenzo-*p*-dioxins from some polychlorinated biphenyls by chromatography on an aluminum oxide column. *J. Assoc. Off. Anal. Chem.* 54: 1426.
4. Jensen, S. et al. 1969. DDT and PCB in marine animals from Swedish waters. *Nature* 224: 247.
5. Risebrough, R. 1969. Chlorinated hydrocarbons in marine ecosystems. In: M. W. Miller and G. G. Berg (eds.). *Chemical Fallout*. Charles C. Thomas, Springfield, Illinois.
6. Prestt, I., Jeffries, D. J. and Moore, N. W. 1970. Polychlorinated biphenyls in wild birds in Britain and their avian toxicity. *Environ. Pollut.* 1: 3.
7. Reynolds, L. M. 1971. Pesticide residue analysis in the presence of polychlorobiphenyls (PCBs). *Residue Reviews* 34: 27.